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(54) Method of laundering fabric

(57) A method of laundering fabric onto which a cationic fabric softening active has been deposited and dried comprising the step of contacting the fabric with an aqueous wash liquor having the following composition:
a) 15 to 600 ppm non-soap surfactant,
b) at least 50 ppm ethoxylated polyethylene imine,
c) at least 25 ppm polyester soil release polymer,
the total level of polymer (b+ c) being at least 20 wt% of the level of non soap surfactant (a),
d) 0.1 to 100 ppm enzyme selected from protease, amylase, cellulase,
e) optionally, lipase enzyme.

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Description

TECHNICAL FIELD

[0001] This invention relates to a method of laundering fabric onto which a quaternary ammonium fabric softening compound has been deposited and dried.

BACKGROUND

[0002] Cationic rinse conditioners are known to exhaust almost completely onto fabrics during the rinsing process. It is known, for example from "Liquid detergents", published 2006, CRC press page 490, that anionic surfactants will complex with cationic actives and that the resulting complex may deposit onto fabrics and, as a result, the stain removal performance of detergent products comprising anionic surfactant may be reduced. At lower in-wash surfactant levels it is expected that this loss of performance will become more significant. This expectation is supported by the teaching in WO93/018124 (P&G) which, although relating mainly to granular detergent compositions, should be expected to apply also to liquids because the effect occurs in-wash. This document states that there is interest in the development of detergent compositions which include a surfactant system comprising only low levels of anionic surfactant. According to WO93/018124 a disadvantage of formulating such compositions is that detergency performance may be impaired by the large degree of complexation of the low level of anionic surfactants by any cationic fabric softener components which may be present in the wash solution. Such cationic fabric softener components may be introduced into the wash solution as residues on the fabrics to be washed resulting from previous treatment of the fabric with a fabric conditioning composition containing such cationic softener components.

[0003] WO93/018124 claims a detergent composition comprising low levels (5% to 10% combined weight) of a combination of water soluble alkyl ethoxysulphate anionic surfactant and alkyl sulphate anionic surfactant in combination at specific weight ratios. Although this document discloses "robust detergency performance", of the composition even in the presence of cationic fabric softener components in the wash solution, the examples use an imidazoline based cationic fabric conditioner and show reduced yellowing (whiteness loss) rather than improved soil (stain) removal. It is well documented that imidazoline actives have yellowing issues (see. Levinson. J. Surfactants and Detergents vol 2 (2) 223-235 (see table 4 p230)). The solution to this problem by use of alkyl sulphates is known from US 3 644 203, where it is taught that the anti-yellowing effect is due to the complexation of the alkyl sulphate with the cationic fabric softener in the composition (in the presence of further ingredients). The development in WO93/018124 seems to be to form the anti-yellowing complex by utilisation the alky sulphate or alkyl ether sulphate anionic surfactant carried over from the main wash to the rinse.

[0004] WO2009/153184 describes a method of laundering fabrics that uses very low levels of in-wash surfactant, preferably comprising anionic surfactant. Wash performance is boosted by inclusion of high levels of specific polymers and enzymes. The skilled person would expect that compositions delivering such low in-wash levels of anionic surfactant would be more affected by the carry over of cationic on the fabric from previous washes/rinses than compositions and laundry processes which deliver higher levels of in-wash anionic surfactant.

[0005] Surprisingly, we have discovered that when using the compositions and method described in WO2009/153184 a much smaller reduction in wash performance occurs on fabric treated with cationic rinse conditioner than the effect observed for prior art detergent liquids, even those that contain the water soluble alkyl ethoxysulphate claimed to improve detergency in WO93/018124.

[0006] In the art it taught to formulate some laundry detergents with mixtures of anionic and cationic surfactants (usually less of the latter). The cationic is typically used to modify the packing behaviour of the surfactant system to make it more lamellar. Rinse conditioner cationic actives, including imidazoline actives, typically have two long alkyl chains and these do not exhibit the same composition benefits as cationic surfactants with one (usually shorter) fatty alkyl chain.

[0007] Fabric conditioner is widely used by consumers. It would be advantageous to identify a washing composition that could be used in a laundry detergent process such that the wash performance is less compromised by previous use of a fabric conditioner.

SUMMARY OF THE INVENTION

[0008] According to the present invention there is provided a method of laundering fabric onto which a cationic fabric softening active has been deposited and dried comprising the step of contacting the fabric with an aqueous wash liquor having the following composition:

a) 15 to 600 ppm non-soap surfactant,
b) at least 50 ppm ethoxylated polyethylene imine,

c) at least 25 ppm polyester soil release polymer,
the total level of polymer (b+ c) being at least 20 wt% of the level of non soap surfactant (a),
d) 0.1 to 100 ppm enzyme selected from protease, amylase, cellulase,
e) optionally, lipase enzyme.

[0009] Preferably the level of non-soap surfactant (a) is from 200 to 400 ppm. Typically the non-soap surfactant (a) comprises at least 50 ppm of anionic surfactant.

[0010] Advantageously the EPEI is nonionic. The cationic fabric softening active is preferably a quaternary ammonium compound.

[0011] The polyester soil release polymer (c) is preferably nonionic and most preferably comprises a polyester substantive midblock of terephthalate repeat units and one or more end blocks of polyethylene glycol capped with a lower alkyl or hydrogen moiety.

[0012] The wash liquor may be formed by dosing 15 to 40 ml of an aqueous liquid detergent composition to water and diluting by a factor of at least 600.

[0013] The non-soap surfactant most preferably comprises linear alkyl benzene sulphonate (LAS), sodium lauryl ether sulphate (SLES) and ethoxylated fatty alcohol nonionic, even more preferably the non-soap surfactant further comprises carbobetaine.

[0014] The low surfactant composition used in this method may still suffer a reduction in detergency performance on some stains when the load to be washed has been pre-exposed to rinse conditioner. However, surprisingly, this reduction is much smaller relative to the losses noted for prior art detergent liquids used at their recommended doses. This is surprising because it was expected that higher detergent levels would lead to less effect and lowering of the in-wash detergent levels, particularly anionic detergent levels would increase any problems caused by cationic rinse conditioner carry over.

DETAILED DESCRIPTION OF THE INVENTION

[0015] To form the wash liquor for use in the method according to the invention a concentrated laundry liquid with lower than expected levels of surfactant is used as described in WO2009/153184. Thus in one embodiment a low volume, less than 25 ml and preferably around 20 ml of the concentrated liquid is dosed to a wash load and diluted with water to form the wash liquor for use in the process. Although the exact dilution will vary from load to load and from one washing machine to another it is expected suitable compositions for use in the process according to the invention may comprise the ingredients described below at the levels detailed below.

The detergent liquids

[0016] The compositions for use in the method of the invention comprise detersive surfactant. The non soap detersive surfactant makes up at least 10 wt% of the liquid composition, preferably it makes up from 12 to 60 wt%. The compositions for use according to the invention most preferably have total active detersive surfactant levels of at least 15 wt%.

[0017] In the method the compositions are used in small doses that require them to be diluted in at least 500 times their own volume of water to form a main-wash liquor comprising at most 0.5 g/l surfactant. They may be concentrated compositions designed for front loading automatic washing machines, hand washing or top loading automatic washing machines. In hand washing less water may be used and in top loading automatic washing machines a higher amount of water would normally be used than fro a front loading automatic machine. The dose of detergent liquid is adjusted accordingly to give similar wash liquor concentrations.

Surfactants

[0018] Surfactants assist in removing soil from the textile materials and also assist in maintaining removed soil in solution or suspension in the wash liquor. Anionic, or blends of anionic and nonionic, surfactants are a preferred feature of the present invention. The amount of anionic surfactant is preferably at least 5 wt%. Preferably, anionic surfactants form the majority of the non-soap surfactant (a).

Anionic Surfactants

[0019] Preferred alkyl sulphonates are alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates (LAS) having an alkyl chain length of C_8-C_{15}. The counter ion for anionic surfactants is generally an alkali metal, typically sodium, although other counter-ions such as MEA, TEA or ammonium can be used. Suitable anionic surfactant materials are available in the marketplace as the 'Genapol'™ range from Clariant. Preferred linear alkyl benzene sulphonate surfactants are Detal LAS with an alkyl chain length of from 8 to 15, more preferably 12 to 14.

[0020] It is desirable that the composition further comprises an alkyl polyethoxylate sulphate anionic surfactant of the formula (I):

$$RO(C_2H_4O)_xSO_3^-M^+ \qquad (I)$$

where R is an alkyl chain having from 10 to 22 carbon atoms, saturated or unsaturated, M is a cation which makes the compound water-soluble, especially an alkali metal, ammonium or substituted ammonium cation, and x averages from 1 to 15.

[0021] Preferably R is an alkyl chain having from 12 to 16 carbon atoms, M is Sodium and x averages from 1 to 3, preferably x is 3; This is the anionic surfactant sodium lauryl ether sulphate (SLES). It is the sodium salt of lauryl ether sulphonic acid in which the predominantly C12 lauryl alkyl group has been ethoxylated with an average of 3 moles of ethylene oxide per mole.

[0022] Although less preferred, some alkyl sulphate surfactant (PAS) may be used, especially the non-ethoxylated C_{12-15} primary and secondary alkyl sulphates. A particularly preferred material, commercially available from Cognis, is Sulphopon 1214G.

[0023] PAS is preferably used in admixture with LAS and most preferably in admixture with LAS and SLES. A preferred SLES/AO/LAS/PAS liquid has a detersive surfactant system comprising 60 parts SLES, 20 parts amine oxide, 10 parts LAS and 10 parts PAS.

Nonionic Surfactants

[0024] Nonionic surfactants include primary and secondary alcohol ethoxylates, especially C_8-C_{20} aliphatic alcohol ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C_{10}-C_{15} primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkyl polyglycosides, glycerol monoethers and polyhydroxy amides (glucamide). Mixtures of nonionic surfactant may be used. When included therein the composition contains from 0.2 wt% to 40 wt%, preferably 1 wt% to 20 wt%, more preferably 5 to 15 wt% of a non-ionic surfactant, such as alcohol ethoxylate, nonylphenol ethoxylate, alkylpolyglycoside, alkyldimethylamineoxide, ethoxylated fatty acid monoethanolamide, fatty acid monoethanolamide, polyhydroxy alkyl fatty acid amide, or N-acyl N-alkyl derivatives of glucosamine ("glucamides").

[0025] Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C_8-C_{20} aliphatic alcohols ethoxylated with an average of from 1 to 35 moles of ethylene oxide per mole of alcohol, and more especially the C_{10}-C_{15} primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol.

Amine Oxide Surfactants

[0026] The composition may comprise up to 10 wt% of an amine oxide of the formula (2):

$$R^1N(O)(CH_2R^2)_2 \qquad (2)$$

[0027] In which R^1 is a long chain moiety and each CH_2R^2 is a short chain moiety. R^2 is preferably selected from hydrogen, methyl and $-CH_2OH$. In general R^1 is a primary or branched hydrocarbyl moiety which can be saturated or unsaturated, preferably, R^1 is a primary alkyl moiety. R^1 is a hydrocarbyl moiety having chain length of from about 8 to about 18.

[0028] In preferred amine oxides R^1 is C_8-C_{18} alkyl, and R^2 is H. These amine oxides are illustrated by C_{12-14} alkyldimethyl amine oxide, hexadecyl dimethylamine oxide, octadecylamine oxide.

[0029] A preferred amine oxide material is Lauryl dimethylamine oxide, also known as dodecyldimethylamine oxide or DDAO. Such an amine oxide material is commercially available from Hunstman under the trade name Empigen® OB.

[0030] Amine oxides suitable for use herein are also available from Akzo Chemie and Ethyl Corp. See McCutcheon's compilation and Kirk-Othmer review article for alternate amine oxide manufacturers.

[0031] Whereas in certain of the preferred embodiments R^2 is H, it is possible for R^2 to be a moiety larger than H. Specifically, R^2 may be CH_2OH, such as: hexadecylbis(2-hydroxyethyl)amine oxide, tallowbis(2-hydroxyethyl)amine oxide, stearylbis(2-hydroxyethyl)amine oxide and oleylbis(2- hydroxyethyl)amine oxide.

[0032] Preferred amine oxides have the formula (3):

$$O^- - N^+(Me)_2R^1 \qquad (3)$$

where R^1 is C_{12-16} alkyl, preferably C_{12-14} alkyl; Me is a methyl group.

Zwitterionic Surfactants

[0033] Nonionic-free systems with up to 95 %wt LAS can be made provided that some zwitterionic surfactant, such as sulphobetaine, is present. A preferred zwitterionic material is a betaine available from Huntsman under the name Empigen® BB. Betaines, improve particulate soil detergency in the compositions of the invention.

Cationic Surfactants

[0034] Cationic surfactants are preferably substantially absent.

Soap

[0035] The compositions may comprise soap which can act as a builder and/or as an antifoam. The amount of non-soap anionic surfactant must exceed the amount of soap. The amount of soap must be less than or equal to 15wt% of the total liquid composition.

Polymers

EPEI

[0036] The composition comprises an ethoxylated polyethyleneimine polymer (EPEI) for cleaning. Preferably the EPEI is nonionic. That means it does not have any quaternary nitrogens, or nitrogen oxides or any ionic species other than possible pH affected protonation of nitrogens.

[0037] Polyethylene imines (PEIs, especially modified PEIs) are materials composed of ethylene imine units -CH2CH2NH- and, where branched, the hydrogen on the nitrogen is replaced by another chain of ethylene imine units. These polyethyleneimines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulphite, sulphuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, and the like. Specific methods for preparing these polyamine backbones are disclosed in U.S. Pat. No. 2,182,306, Ulrich et al., issued Dec. 5, 1939; U.S. Pat. No. 3,033,746, Mayle et al., issued May 8, 1962; U.S. Pat. No. 2,208,095, Esselmann et al., issued Jul. 16, 1940; U.S. Pat. No. 2,806,839, Crowther, issued Sep. 17, 1957; U.S. Pat. No. 2,553,696, Wilson, issued May 21, 1951 and WO2006/086492 (BASF).

[0038] Preferably, the EPEI comprises a polyethyleneimine backbone wherein the modification of the polyethyleneimine backbone is intended to leave the polymer without quaternisation. Such nonionic EPEI may be represented as PEI(X)YEO where X represents the molecular weight of the unmodified PEI and Y represents the average moles of ethoxylation per nitrogen atom in the polyethyleneimine backbone. The ethoxylation number Y may range from 9 to 40 ethoxy moieties per modification, preferably it is in the range of 16 to 26, most preferably 18 to 22. X is selected to be from about 300 to about 10000 weight average molecular weight and is preferably about 600.

[0039] The ethoxylated polyethyleneimine polymer (EPEI) is present in the composition preferably at a level of between 0.01 and 25 wt%, but more preferably at a level of at least 2 wt% and/or less than 9.5 wt%, most preferably from 3 to 9 wt% and with a ratio of non-soap surfactant to EPEI of from 2:1 to 7:1, preferably from 3:1 to 6:1, or even to 5:1.

Soil Release Polymer

[0040] The composition comprises at least 0.5 wt% of a soil release polymer for oily soil removal, especially from polyester.

[0041] Soil release polymers improve the main wash performance of the compositions when used in the low in wash surfactant process of the present invention.

[0042] One preferred class of polymer is the fabric-substantive polymers comprising at least one of (i) saccharide or (ii) dicarboxylic acid and polyol monomer units. Typically these have soil release properties and while they can have a primary detergency effect they generally assist in subsequent cleaning. Preferably these should be present at a level of at least 2% wt preferably at least 3 wt% of the composition.

[0043] The soil release polymer will generally comprise up to 10.0 wt%, of the detergent composition, preferably from

3 wt% to 9 wt%, but more preferably they are used at greater than 2 wt% and most preferably greater than 3 wt%, even more preferably greater than 5 wt%, say 6 to 8 wt% in the composition.

[0044] Generally the soil release polymers for polyester will comprise polymers of aromatic dicarboxylic acids and alkylene glycols (including polymers containing polyalkylene glycols).

[0045] The polymeric soil release agents useful herein especially include those soil release agents having:

(a) one or more nonionic hydrophilic components consisting essentially of:

(i) polyoxyethylene segments with a degree of polymerization of at least 2, or

(ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophilic segment does not encompass any oxypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or

(iii) a mixture of oxyalkylene units comprising oxyethylene and from 1 to about 30 oxypropylene units wherein said mixture contains a sufficient amount of oxyethylene units such that the hydrophilic component has hydrophilicity great enough to increase the hydrophilicity of conventional polyester synthetic fibre surfaces upon deposit of the soil release agent on such surface, said hydrophilic segments preferably comprising at least about 25% oxyethylene units and more preferably, especially for such components having about 20 to 30 oxypropylene units, at least about 50% oxyethylene units; or

(b) one or more hydrophobic components comprising:

(i) C_3 oxyalkylene terephthalate segments, wherein, if said hydrophobic components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate: C_3 oxyalkylene terephthalate units is about 2:1 or lower,

(ii) C_4-C_6 alkylene or oxy C_4-C_6 alkylene segments, or mixtures therein,

(iii) poly (vinyl ester) segments, preferably polyvinyl acetate), having a degree of polymerization of at least 2, or (iv) C_1-C_4 alkyl ether or C_4 hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C_1-C_4 alkyl ether or C_4 hydroxyalkyl ether cellulose derivatives, or mixtures therein, and such cellulose derivatives are amphiphilic, whereby they have a sufficient level of C_1-C_4 alkyl ether and/or C_4 hydroxyalkyl ether units to deposit upon conventional polyester synthetic fibre surfaces and retain a sufficient level of hydroxyls, once adhered to such conventional synthetic fibre surface, to increase fibre surface hydrophilicity, or a combination of (a) and (b).

[0046] Typically, the polyoxyethylene segments of (a)(i) will have a degree of polymerization of from about 200, although higher levels can be used, preferably from 3 to about 150, more preferably from 6 to about 100. Suitable oxy C_4-C_6 alkylene hydrophobic segments include, but are not limited to, end-caps of polymeric soil release agents such as $MO_3\ S(CH_2)_n\ OCH_2\ CH_2\ O$--, where M is sodium and n is an integer from 4-6, as disclosed in U.S. Pat. No. 4,721,580, issued Jan. 26, 1988 to Gosselink.

[0047] Soil release agents characterized by poly(vinyl ester) hydrophobic segments include graft copolymers of poly (vinyl ester), e.g., C_1-C_6 vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones. See European Patent Application 0 219 048, published Apr. 22, 1987 by Kud, et al. Commercially available soil release agents of this kind include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West Germany).

[0048] One type of preferred soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Pat. No. 3,959,230 to Hays, issued May 25, 1976 and U.S. Pat. No. 3,893,929 to Basadur issued Jul. 8, 1975.

[0049] Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units contains 10 to 15 wt% of ethylene terephthalate units together with 90 to 80 wt% weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Examples of this polymer include the commercially available material ZELCON 5126 (from DuPont) and MILEASE T (from ICI). See also U.S. Pat. No. 4,702,857, issued Oct. 27, 1987 to Gosselink.

[0050] Another preferred polymeric soil release agent is a sulphonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties covalently attached to the backbone. These soil release agents are described fully in U.S. Pat. No. 4,968,451, issued

Nov. 6, 1990 to J.J. Scheibel and E. P. Gosselink. Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. Pat. No. 4,711,730, issued Dec. 8, 1987 to Gosselink et al, the anionic end-capped oligomeric esters of U.S. Pat. No. 4,721,580, issued Jan. 26, 1988 to Gosselink, and the block polyester oligomeric compounds of U.S. Pat. No. 4,702,857, issued Oct. 27, 1987 to Gosselink.

[0051] Preferred polymeric soil release agents also include the soil release agents of U.S. Pat. No. 4,877,896, issued Oct. 31, 1989 to Maldonado et al, which discloses anionic, especially sulfoarolyl, end-capped terephthalate esters.

[0052] Still another preferred soil release agent is an oligomer with repeat units of terephthaloyl units, sulfoisoterephthaloyl units, oxyethyleneoxy and oxy-1,2-propylene units. The repeat units form the backbone of the oligomer and are preferably terminated with modified isethionate end-caps. A particularly preferred soil release agent of this type comprises about one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a ratio of from about 1.7 to about 1.8, and two end-cap units of sodium 2-(2-hydroxyethoxy)-ethanesulphonate. Said soil release agent also comprises from about 0.5% to about 20%, by weight of the oligomer, of a crystalline-reducing stabilizer, preferably selected from the group consisting of xylene sulfonate, cumene sulfonate, toluene sulfonate, and mixtures thereof.

[0053] Suitable soil release polymers are described in WO 2008095626 (Clariant); WO 2006133867 (Clariant); WO 2006133868 (Clariant); WO 2005097959 (Clariant); WO 9858044 (Clariant); WO 2000004120 (Rhodia Chimie); US 6242404 (Rhodia Inc); WO 2001023515 (Rhodia Inc); WO 9941346 (Rhodia Chim); WO 9815346 (Rhodia Inc); WO 9741197 (BASF); EP 728795 (BASF); US 5008032 (BASF); WO 2002077063 (BASF); EP 483606 (BASF); EP 442101 (BASF); WO 9820092 (Proctor & Gamble); EP 201124 (Proctor & Gamble); EP 199403 (Proctor & Gamble); DE 2527793 (Proctor & Gamble); WO 9919429 (Proctor & Gamble); WO 9859030 (Proctor & Gamble); US 5834412 (Proctor & Gamble); WO 9742285 (Proctor & Gamble); WO 9703162 (Proctor & Gamble); WO 9502030 (Proctor & Gamble); WO 9502028 (Proctor & Gamble); EP 357280 (Proctor & Gamble); US 4116885 (Proctor & Gamble); WO 9532232 (Henkel); WO 9532232 (Henkel); WO 9616150 (Henkel); WO 9518207 (Henkel); EP 1099748 (Henkel); FR 2619393 (Colgate Palmolive); DE 3411941 (Colgate Palmolive); DE 3410810 (Colgate Palmolive); WO 2002018474 (RWE-DEA MINERALOEL & CHEM AG; SASOL GERMANY GMBH); EP 743358 (Textil Color AG); PL 148326 (Instytut Ciezkiej Syntezy Organicznej "Blachownia", Pol.); JP 2001181692 (Lion Corp); JP 11193397 A (Lion Corp); RO 114357 (S.C. "Prod Cresus" S.A., Bacau, Rom.); and US 7119056 (Sasol).

[0054] Particularly preferred are combinations of relatively high levels of EPEI, particularly greater than 2.5 wt% based on the composition, with soil release polymers. We have determined that combination of EPEI and soil release polymers of the above types enables increased performance at lower surfactant levels compared to 1.0g/L or higher non-soap surfactant wash liquors without either EPEI or SRP. This effect is particularly visible on a range of stains on polyester, most particularly red clay. The effect of the combination on sunflower oil and foundation is also beneficial. SRP performance is enhanced significantly by repeated pre-treatment. There is some evidence of a build-up effect of EPEI performance. Preferred EPEI is nonionic, most preferably it comprises no propoxy moieties.

[0055] The most preferred soil release polymers are the water soluble/miscible or dispersible polyesters such as: linear polyesters sold under the Repel-O-Tex brand by Rhodia (Gerol), or the Texcare brand by Clariant, especially Texcare SRN170, and heavily branched polyesters such as those available from Sasol and described in US 7119056. The polyesters are preferably nonionic and comprise a mid block of spaced apart terephthalate repeat units and at least one end block based on polyethylene glycol with a lower alkyl or hydrogen termination.

Other polymers

[0056] In addition to the essential EPEI and polyester soil release polymer the compositions may further comprise dye transfer inhibition polymers, anti redeposition polymers and cotton soil release polymers, especially those based on modified cellulosic materials.

Enzymes

[0057] It is preferable that at least one or more enzymes may be present in the compositions for cleaning boost.

Lipase

[0058] Lipase is a particularly preferred enzyme. The composition preferably contains from about 5 to about 20000 LU/g of a lipase. Preferred lipase enzymes include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful lipases include lipases from *Humicola,* more preferably ones which comprise a polypeptide having an amino acid sequence which has at least 90% sequence identity with the wild-type lipase derived from *Humicola lanuginose,* most preferably strain DSM 4109. The amount in the composition is higher than typically found in liquid detergents. This can be seen by the ratio of non-soap surfactant to lipase enzyme, in particular. A particularly preferred lipase enzyme is available under the trademark Lipoclean™ from Novozymes.

[0059] As noted above, suitable lipases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful lipases include lipases from *Humicola* (synonym *Thermomyces*), e.g. from *H. lanuginosa* (*T. lanuginosus*) as described in EP 258 068 and EP 305 216 or from *H. insolens* as described in WO 96/13580, a *Pseudomonas* lipase, e.g. from *P. alcaligenes* or *P. pseudoalcaligenes* (EP 218 272), *P. cepacia* (EP 331 376), *P. stutzeri* (GB 1,372,034), *P. fluorescens, Pseudomonas* sp. strain SD 705 (WO 95/06720 and WO 96/27002), *P. wisconsinensis* (WO 96/12012), a *Bacillus* lipase, e.g. from *B. subtilis* (Dartois et al. (1993), Biochemica et Biophysica Acta, 1131, 253-360), *B. stearothermophilus* (JP 64/744992) or *B. pumilus* (WO 91/16422). As noted above the preferred ones have a high degree of homology with the wild-type lipase derived from *Humicola lanuginose.*

[0060] Other examples are lipase variants such as those described in WO 92/05249, WO 94/01541, EP 407 225, EP 260 105, WO 95/35381, WO 96/00292, WO 95/30744, WO 94/25578, WO 95/14783, WO 95/22615, WO 97/04079 and WO 97/07202.

[0061] Preferred commercially available lipase enzymes include Lipolase™ and Lipolase Ultra™, LipeX™ and Lipoclean™ (Novozymes A/S).

[0062] In addition to or as an alternative to lipase one or more other enzymes may be present. However, lipase is particularly preferred.

[0063] Advantageously, the presence of relatively high levels of calcium in the poorly built or unbuilt compositions of the invention has a beneficial effect on the turnover of certain enzymes, particularly lipase enzymes and preferably lipases from *Humicola.*

[0064] The preferred lipases include first wash lipases which comprise a polypeptide having an amino acid sequence which has at least 90% sequence identity with the wild-type lipase derived from *Humicola lanuginosa* strain DSM 4109 and compared to said wild-type lipase, comprises a substitution of an electrically neutral or negatively charged amino acid within 15 A of E1 or Q249 with a positively charged amino acid; and may further comprise:

(I) a peptide addition at the C-terminal;

(II) a peptide addition at the N-terminal;

(III) the following limitations:

  i. comprises a negatively charged amino acid in position E210 of said wild-type lipase;

  ii. comprises a negatively charged amino acid in the region corresponding to positions 90-101 of said wild-type lipase; and

  iii. comprises a neutral or negatively charged amino acid at a position corresponding to N94 of said wild-type lipase; and/or

  iv. has a negative charge or neutral charge in the region corresponding to positions 90-101 of said wild-type lipase; and

  v. mixtures thereof.

[0065] These are available under the Lipex™ brand from Novozymes. A similar enzyme from Novozymes but believed to fall outside of the above definition has been offered by Novozymes under the name Lipoclean™ and this is also preferred.

Phospholipase:

[0066] The method of the invention may be carried out in the presence of phospholipase classified as EC 3.1.1.4 and/or EC 3.1.1.32. As used herein, the term phospholipase is an enzyme which has activity towards phospholipids. Phospholipids, such as lecithin or phosphatidylcholine, consist of glycerol esterified with two fatty acids in an outer (sn-1) and the middle (sn-2) positions and esterified with phosphoric acid in the third position; the phosphoric acid, in turn, may be esterified to an amino-alcohol. Phospholipases are enzymes which participate in the hydrolysis of phospholipids. Several types of phospholipase activity can be distinguished, including phospholipases A_1 and A_2 which hydrolyze one fatty acyl group (in the sn-1 and sn-2 position, respectively) to form lysophospholipid; and lysophospholipase (or phospholipase B) which can hydrolyze the remaining fatty acyl group in lysophospholipid. Phospholipase C and phospholipase D (phosphodiesterases) release diacyl glycerol or phosphatidic acid respectively.

Protease:

[0067] Suitable proteases include those of animal, vegetable or microbial origin. Microbial origin is preferred. Chemically modified or protein engineered mutants are included. The protease may be a serine protease or a metallo protease, preferably an alkaline microbial protease or a trypsin-like protease. Preferred commercially available protease enzymes include Alcalase™, Savinase™, Primase™, Duralase™, Dyrazym™, Esperase™, Everlase™, Polarzyme™, and Kannase™, (Novozymes A/S), Maxatase™, Maxacal™, Maxapem™, Properase™, Purafect™, Purafect OxP™, FN2™, and FN3™ (Genencor International Inc.).

Cutinase:

[0068] The method of the invention may be carried out in the presence of cutinase. classified in EC 3.1.1.74. The cutinase used according to the invention may be of any origin. Preferably cutinases are of microbial origin, in particular of bacterial, of fungal or of yeast origin.

Amylase:

[0069] Suitable amylases (alpha and/or beta) include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Amylases include, for example, alpha-amylases obtained from *Bacillus,* e.g. a special strain of *B. licheniformis,* described in more detail in GB 1,296,839, or the *Bacillus* sp. strains disclosed in WO 95/026397 or WO 00/060060. Commercially available amylases are Duramyl™, Termamyl™, Termamyl Ultra™, Natalase™, Stainzyme™, Fungamyl™ and BAN™ (Novozymes A/S), Rapidase™ and Purastar™ (from Genencor International Inc.).

Cellulase:

[0070] Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Suitable cellulases include cellulases from the genera *Bacillus, Pseudomonas, Humicola, Fusarium, Thielavia, Acremonium,* e.g. the fungal cellulases produced from *Humicola insolens, Thielavia terrestris, Myceliophthora thermophila,* and *Fusarium oxysporum* disclosed in US 4,435,307, US 5,648,263, US 5,691,178, US 5,776,757, WO 89/09259, WO 96/029397, and WO 98/012307. Commercially available cellulases include Celluzyme™, Carezyme™, Endolase™, Renozyme™ (Novozymes A/S), Clazinase™ and Puradax HA™ (Genencor International Inc.), and KAC-500(B)™ (Kao Corporation).

Peroxidases/oxidases:

[0071] Suitable peroxidases/oxidases include those of plant, bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful peroxidases include peroxidases from *Coprinus,* e.g. from *C. cinereus,* and variants thereof as those described in WO 93/24618, WO 95/10602, and WO 98/15257. Commercially available peroxidases include Guardzyme™ and Novozym™ 51004 (Novozymes A/S).

Pectate Lyases:

[0072] Pectate lyases (also called polygalacturonate lyases): Examples of pectate lyases include pectate lyases that have been cloned from different bacterial genera such as Erwinia, Pseudomonas, Klebsiella and Xanthomonas, as well as from Bacillus subtilis (Nasser et al. (1993) FEBS Letts. 335:319-326) and Bacillus sp. YA-14 (Kim et al. (1994) Biosci. Biotech. Biochem. 58:947-949). Purification of pectate lyases with maximum activity in the pH range of 8-10 produced by Bacillus pumilus (Dave and Vaughn (1971) J. Bacteriol. 108:166-174), B. polymyxa (Nagel and Vaughn (1961) Arch. Biochem. Biophys. 93:344-352), B. stearothermophilus (Karbassi and Vaughn (1980) Can. J. Microbiol. 26:377-384), Bacillus sp. (Hasegawa and Nagel (1966) J. Food Sci. 31:838-845) and Bacillus sp. RK9 (Kelly and Fogarty (1978) Can. J. Microbiol. 24:1164-1172) have also been described. Any of the above, as well as divalent cation-independent and/or thermostable pectate lyases, may be used in practicing the invention. In preferred embodiments, the pectate lyase comprises the pectate lyase disclosed in Heffron et al., (1995) Mol. Plant-Microbe Interact. 8: 331-334 and Henrissat et al., (1995) Plant Physiol. 107: 963-976. Specifically contemplated pectatel lyases are disclosed in WO 99/27083 and WO 99/27084. Other specifically contemplated pectate lyases (derived from Bacillus licheniformis) are disclosed in US patent no. 6,284,524 (which document is hereby incorporated by reference). Specifically contemplated pectate lyase variants are disclosed in WO 02/006442, especially the variants disclosed in the Examples in WO 02/006442 (which document is hereby incorporated by reference). Examples of commercially available alkaline pectate lyases include BIOPREP™ and SCOURZYME™ L from Novozymes A/S, Denmark.

Mannanases:

[0073] Mannanase: Examples of mannanases (EC 3.2.1.78) include mannanases of bacterial and fungal origin. In a specific embodiment the mannanase is derived from a strain of the filamentous fungus genus Aspergillus, preferably Aspergillus niger or Aspergillus aculeatus (WO 94/25576). WO 93/24622 discloses a mannanase isolated from Trichoderma reseei. Mannanases have also been isolated from several bacteria, including Bacillus organisms. For example, Talbot et al., Appl. Environ. Microbiol., Vol.56, No. 11, pp. 3505-3510 (1990) describes a beta-mannanase derived from Bacillus stearothermophilus. Mendoza et al., World J. Microbiol. Biotech., Vol. 10, No. 5, pp. 551-555 (1994) describes a beta-mannanase derived from Bacillus subtilis. JP-A-03047076 discloses a beta-mannanase derived from Bacillus sp. JP-A-63056289 describes the production of an alkaline, thermostable beta-mannanase. JP-A-63036775 relates to the Bacillus microorganism FERM P-8856 which produces beta-mannanase and beta-mannosidase. JP-A-08051975 discloses alkaline beta-mannanases from alkalophilic Bacillus sp. AM-001. A purified mannanase from Bacillus amyloliquefaciens is disclosed in WO 97/11164. WO 91/18974 describes a hemicellulase such as a glucanase, xylanase or mannanase active. Contemplated are the alkaline family 5 and 26 mannanases derived from Bacillus agaradhaerens, Bacillus licheniformis, Bacillus halodurans, Bacillus clausii, Bacillus sp., and Humicola insolens disclosed in WO 99/64619. Especially contemplated are the Bacillus sp. mannanases concerned in the Examples in WO 99/64619.

[0074] Examples of commercially available mannanases include Mannaway™ available from Novozymes A/S Denmark.

[0075] The enzyme and any perfume/fragrance or pro-fragrance present may show some interaction and should be chosen such that this interaction is not negative. Some negative interactions may be avoided by encapsulation of one or other of enzyme and pro-fragrance and/or other segregation within the product.

Enzyme Stabilizers

[0076] Any enzyme present in the composition may be stabilized using conventional stabilizing agents, e.g., a polyol such as propylene glycol or glycerol, a sugar or sugar alcohol, lactic acid, boric acid, or a boric acid derivative, e.g., an aromatic borate ester, or a phenyl boronic acid derivative such as 4-formylphenyl boronic acid, and the composition may be formulated as described in e.g. WO 92/19709 and WO 92/19708.

Further Optional Ingredients

[0077] The compositions of the invention may contain one or more other ingredients. Such ingredients include viscosity modifiers, foam boosting agents, preservatives (e.g. bactericides), pH buffering agents, polyelectrolytes, anti-shrinking agents, anti-wrinkle agents, anti-oxidants, sunscreens, anti-corrosion agents, drape imparting agents, anti-static agents and ironing aids. The compositions may further comprise, colorants, pearlisers and/or opacifiers, and shading dye.

Fluorescent Agents

[0078] It may be advantageous to include fluorescer in the compositions. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts. The total amount of the fluorescent agent or agents used in the composition is generally from 0.005 to 2 wt %, more preferably 0.01 to 0.5 wt %.

[0079] Preferred classes of fluorescer are: Di-styryl biphenyl compounds, e.g. Tinopal (Trade Mark) CBS-X, Di-amine stilbene di-sulphonic acid compounds, e.g. Tinopal DMS pure Xtra and Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN.

[0080] Preferred fluorescers are: sodium 2 (4-styryl-3-sulfophenyl)-2H-napthol[1,2-d]triazole, disodium 4,4'-bis{[(4-anilino-6-(N methyl-N-2 hydroxyethyl) amino 1,3,5-triazin-2-yl)]amino}stilbene-2-2' disulfonate, disodium 4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino} stilbene-2-2' disulfonate, and disodium 4,4'-bis(2-sulfoslyryl)biphenyl.

Bleach Catalysts

[0081] Detergent compositions according to the invention may comprise a weight efficient bleach system. Such systems typically do not utilise the conventional percarbonate or peracid and/or bleach activator approach.

[0082] The present invention may be used in a formulation that is used to bleach via air, or an air bleach catalyst system. Suitable complexes and organic molecule (ligand) precursors for forming complexes are available to the skilled worker, for example, from: WO 98/39098; WO 98/39406, WO 97/48787, WO 00/29537; WO 00/52124, and WO00/6004 incorporated by reference. An example of a preferred catalyst is a transition metal complex of MeN4Py ligand (N,N-bis (pyridin-2-yl-methyl)-1-,1-bis(pyridin-2-yl)-1-aminoethane). Suitable bispidon catalyst materials and their action are described in WO02/48301.

[0083] Photobleaches may also be employed. In the context of the present invention a "photobleach" is any chemical species that forms a reactive bleaching species on exposure to sunlight, and preferably is not permanently consumed in the reaction. Preferred photo-bleaches include singlet oxygen photo-bleaches and radical photo-bleaches. Suitable singlet oxygen photo-bleaches may be selected from, water soluble phthalocyanine compounds, particularly metallated phthalocyanine compounds where the metal is Zn or Al-Z1 where Z1 is a halide, sulphate, nitrate, carboxylate, alkanolate or hydroxyl ion. Preferably the phthalocyanin has 1-4 SO_3X groups covalently bonded to it where X is an alkali metal or ammonium ion. Such compounds are described in WO2005/014769 (Ciba).

[0084] When present, the bleach catalyst is typically incorporated at a level of about 0.0001 to about 10wt%, preferably about 0.001 to about 5wt%.

Perfume

[0085] Given that the composition of the present invention is designed to be used at very low levels of product dosage, it is advantageous to ensure that perfume is employed efficiently.

[0086] A particularly preferred way of ensuring that perfume is employed efficiently is to use an encapsulated perfume. Use of a perfume that is encapsulated reduces the amount of perfume vapour that is produced by the composition before it is diluted. This is important when the perfume concentration is increased to allow the amount of perfume per wash to be kept at a reasonably high level.

[0087] It is even more preferable that the perfume is not only encapsulated but also that the encapsulated perfume is provided with a deposition aid to increase the efficiency of perfume deposition and retention on fabrics. The deposition aid is preferably attached to the encapsulate by means of a covalent bond, entanglement or strong adsorption, preferably by a covalent bond or entanglement.

Shading dyes

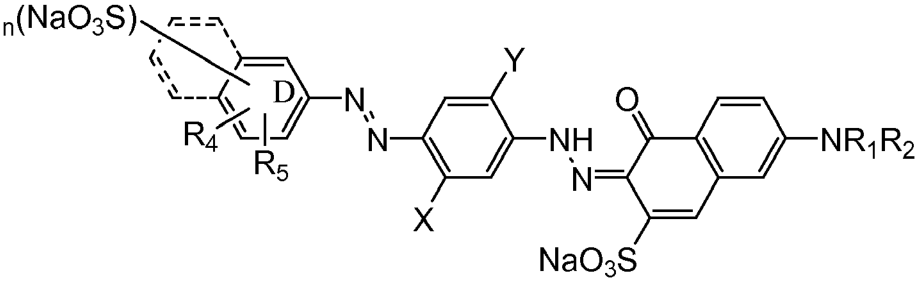
[0088] Shading dye can be used to improve the performance of the compositions used in the method of the present invention. The deposition of shading dye onto fabric is improved when they are used in compositions of the invention and according to the process of the invention. Preferred dyes are violet or blue. It is believed that the deposition on fabrics of a low level of a dye of these shades, masks yellowing of fabrics. A further advantage of shading dyes is that they can be used to mask any yellow tint in the composition itself.

[0089] Suitable and preferred classes of dyes are disclosed below:

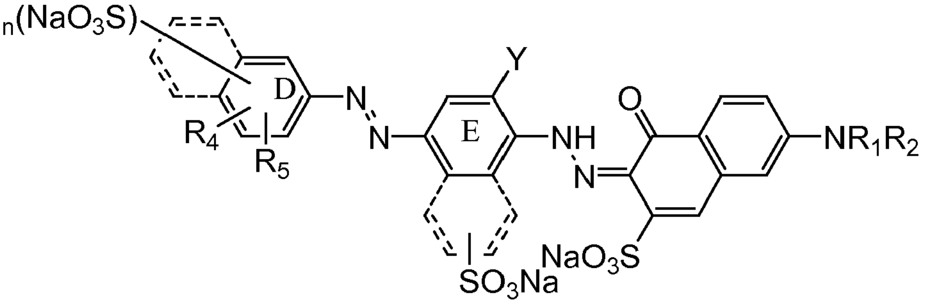
Direct Dyes:

[0090] Direct dyes (otherwise known as substantive dyes) are the class of water soluble dyes which have an affinity for fibres and are taken up directly. Direct violet and direct blue dyes are preferred. Preferably bis-azo or tris-azo dyes are used.

[0091] Most preferably, the direct dye is a direct violet of the following structures:



or



wherein:

ring D and E may be independently naphthyl or phenyl as shown;
R_1 is selected from: hydrogen and C_1-C_4-alkyl, preferably hydrogen;
R_2 is selected from: hydrogen, C_1-C_4-alkyl, substituted or unsubstituted phenyl and substituted or unsubstituted naphthyl, preferably phenyl;
R_3 and R_4 are independently selected from: hydrogen and C_1-C_4-alkyl, preferably hydrogen or methyl;
X and Y are independently selected from: hydrogen, C_1-C_4-alkyl and C_1-C_4-alkoxy; preferably the dye has X= methyl; and, Y = methoxy and n is 0, 1 or 2, preferably 1 or 2.

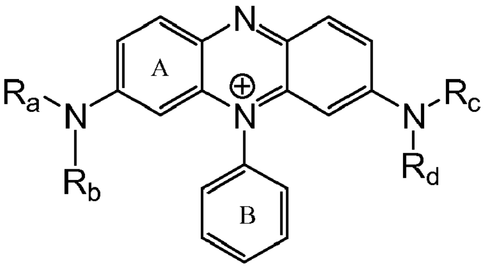
[0092] Preferred dyes are direct violet 7, direct violet 9, direct violet 11, direct violet 26, direct violet 31, direct violet 35, direct violet 40, direct violet 41, direct violet 51, and direct violet 99. Bis-azo copper containing dyes such as direct violet 66 may be used. The benzidene based dyes are less preferred. In another embodiment the direct dye may be covalently linked to the photo-bleach, for example as described in WO2006/024612.
[0093] Preferably the direct dye is present at 0.000001 to 1 wt% more preferably 0.00001 wt% to 0.0010 wt% of the composition.

Acid dyes:

[0094] Cotton substantive acid dyes give benefits to cotton containing garments. Preferred dyes and mixes of dyes are blue or violet. Preferred acid dyes are:

(i) azine dyes, wherein the dye is of the following core structure:

[0095]



wherein R_a, R_b, R_c and R_d are selected from: H, a branched or linear C1 to C7-alkyl chain, benzyl a phenyl, and a naphthyl;
the dye is substituted with at least one SO_3^- or-COO^- group;
the B ring does not carry a negatively charged group or salt thereof;
and the A ring may further substituted to form a naphthyl;
the dye is optionally substituted by groups selected from: amine, methyl, ethyl, hydroxyl, methoxy, ethoxy, phenoxy, Cl, Br, I, F, and NO_2.
[0096] Preferred azine dyes are: acid blue 98, acid violet 50, and acid blue 59, more preferably acid violet 50 and acid blue 98. Other preferred non-azine acid dyes are acid violet 17, acid black 1 and acid blue 29.
[0097] Preferably the acid dye is present at 0.0005 wt% to 0.01 wt% of the formulation.

Hydrophobic dyes:

[0098] The composition may comprise one or more hydrophobic dyes selected from benzodifuranes, methine, triphenylmethanes, napthalimides, pyrazole, napthoquinone, anthraquinone and mono-azo or di-azo dye chromophores. Hydrophobic dyes are dyes which do not contain any charged water solubilising group. Hydrophobic dyes may be selected from the groups of disperse and solvent dyes. Blue and violet anthraquinone and mono-azo dye are preferred.

[0099] Preferred dyes include solvent violet 13, disperse violet 27 disperse violet 26, disperse violet 28, disperse violet 63 and disperse violet 77.

[0100] Preferably the hydrophobic dye is present at 0.0001 wt% to 0.005 wt% of the formulation.

Basic dyes:

[0101] Basic dyes are organic dyes which carry a net positive charge. They deposit onto cotton. They are of particular utility for used in composition that contain predominantly cationic surfactants. Dyes may be selected from the basic violet and basic blue dyes listed in the Colour Index International. Preferred examples include triarylmethane basic dyes, methane basic dye, anthraquinone basic dyes, basic blue 16, basic blue 65, basic blue 66, basic blue 67, basic blue 71, basic blue 159, basic violet 19, basic violet 35, basic violet 38, basic violet 48; basic blue 3, basic blue 75, basic blue 95, basic blue 122, basic blue 124, basic blue 141.

Reactive dyes:

[0102] Reactive dyes are dyes which contain an organic group capable of reacting with cellulose and linking the dye to cellulose with a covalent bond. They deposit onto cotton.

[0103] Preferably the reactive group is hydrolysed or reactive group of the dyes has been reacted with an organic species such as a polymer, so as to the link the dye to this species. Dyes may be selected from the reactive violet and reactive blue dyes listed in the Colour Index International.

[0104] Preferred examples include reactive blue 19, reactive blue 163, reactive blue 182 and reactive blue, reactive blue 96.

Dye conjugates:

[0105] Dye conjugates are formed by binding direct, acid or basic dyes to polymers or particles via physical forces. Dependent on the choice of polymer or particle they deposit on cotton or synthetics. A description is given in WO2006/055787.

[0106] Particularly preferred dyes are: direct violet 7, direct violet 9, direct violet 11, direct violet 26, direct violet 31, direct violet 35, direct violet 40, direct violet 41, direct violet 51, direct violet 99, acid blue 98, acid violet 50, acid blue 59, acid violet 17, acid black 1, acid blue 29, solvent violet 13, disperse violet 27 disperse violet 26, disperse violet 28, disperse violet 63, disperse violet 77 and mixtures thereof.

[0107] Shading dye can be used in the absence of fluorescer, but it is especially preferred to use a shading dye in combination with a fluorescer, for example in order to reduce yellowing due to chemical changes in adsorbed fluorescer.

Builders and sequestrants

[0108] The detergent compositions may also optionally contain relatively low levels of organic detergent builder or sequestrant material. Examples include the alkali metal, citrates, succinates, malonates, carboxymethyl succinates, carboxylates, polycarboxylates and polyacetyl carboxylates. Specific examples include sodium, potassium and lithium salts of oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid. Other examples are DEQUEST™, organic phosphonate type sequestering agents sold by Monsanto and alkanehydroxy phosphonates.

[0109] Other suitable organic builders include the higher molecular weight polymers and copolymers known to have builder properties. For example, such materials include appropriate polyacrylic acid, polymaleic acid, and polyacrylic/polymaleic acid copolymers and their salts, such as those sold by BASF under the name SOKALAN™.

[0110] If utilized, the organic builder materials may comprise from about 0.5% to 20 wt%, preferably from 1 wt% to 10 wt%, of the composition. The preferred builder level is less than 10 wt% and preferably less than 5 wt% of the composition. A preferred sequestrant is HEDP (1-Hydroxyethylidene -1,1,-diphosphonic acid), for example sold as Dequest 2010. Also suitable but less preferred as it gives inferior cleaning results is Dequest® 2066 (Diethylenetriamine penta(methylene phosphonic acid or Heptasodium DTPMP).

Hydrotropes

[0111] The compositions preferably comprise one or more hydrotopes; although the minimum amount consistent with the need for concentration should be used. Suitable hydrotropes include MPG (monopropylene glycol). This and/or other conventionally employed hydrotropes may be used in the composition at levels of from 2 to 10 wt%. In the context of this invention a hydrotrope is a solvent that is neither water nor conventional surfactant that aids the solubilisation of the surfactants and other components in the aqueous liquid to render it isotropic. In addition to MPG, among suitable hydrotropes there may be mentioned as preferred: glycerol, sodium cumene sulphonate, ethanol, other glycols, e.g. di propylene glycol, diethers and urea.

Buffers

[0112] The presence of some buffer is preferred for pH control; preferred buffers are MEA, and TEA. If present they are preferably used in the composition at levels of from 5 to 15 wt%.

External Structurants

[0113] The compositions may have their rheology modified by use of a material or materials that form a structuring network within the composition. Suitable structurants include hydrogenated castor oil, microfibrous cellulose and natural based structurants such as citrus pulp fibre. Citrus pulp fibre is particularly preferred especially if lipase enzyme is included in the composition.

Visual Cues

[0114] The compositions may, and preferably do, comprise visual cues of solid material that is not dissolved in the composition. Preferably they are used in combination with an external structurant to ensure that they remain in suspension. Preferred visual cues are lamellar cues formed from polymer film and possibly comprising functional ingredients that may not be as stable if exposed to the alkaline liquid. Enzymes and bleach catalysts are examples of such ingredients. Also perfume, particularly microencapsulated perfume.

Packaging and dosing

[0115] The liquids may be packaged as unit doses. To allow greater flexibility in dosing the liquids are preferably supplied in multiuse plastics packs with a top or bottom closure. A dosing system may be supplied with the pack either as a part of the cap or as an integrated system.

Method of use

[0116] Following the teaching in WO2009/153184 the liquids according to the invention may be formulated to allow them to be dosed to a typical front loading automatic washing machine at a dosage level of 20ml. The low in wash surfactant level being compensated by the presence of enzymes, soil release polymer and EPEI together with further optional high efficacy cleaning ingredients, such as enzymes. However, the invention is also suitable for the more conventional dosage levels of about 35 ml. To obtain suitable detergent liquids of this type all that is necessary is to add further water and possibly perfume to the 20ml composition before it is packaged.

Fabric conditioner and fabric

[0117] The effect applies to all types of fabric tested, particularly polyester, cotton and mixtures of those types of fibres or fabrics. The fabric conditioning active may be any of the known cationic softening actives, particularly quaternary ammonium compounds including the biodegradable ester quaternary ammonium actives; preferably hardened tallow triethanolamine quaternary. Fabric conditioners comprising imidazolines will also complex with anionic surfactant and the invention extends also to washing of fabrics that have previously been treated with fabric conditioner comprising this type of fabric conditioning active.

[0118] The invention will now be further described with reference to the following nonlimiting examples.

EXAMPLES

[0119] In the examples the following materials are used:

LAS acid	is C12-14 linear alkylbenzene sulphonic acid.
Fatty acid	is saturated lauric fatty acid Prifac® 5908ex Croda.
SLES 3EO	is sodium lauryl ether sulphate with 3 moles EO.
Empigen® BB	is an alkyl betaine ex Huntsman (Coco dimethyl carbobetaine).
NI 7EO	is C12-15 alcohol ethoxylate 7EO nonionic Neodol® 25-7 (ex Shell Chemicals).
Stenol 1618L	is C16/18 fatty alcohol nonionic ex Cognis.
Genepol C200	is coco 20 EO nonionic ex Clariant.
HTTEAQ	is hardened tallow triethanolamine quaternary (cationic fabric softening active).
MPG	is mono propylene glycol.
TEA	is triethanolamine.
NaOH	is 47% sodium hydroxide solution.
EPEI	is Sokalan HP20 - ethoxylated polyethylene imine cleaning polymer: PEI(600) 20EO ex BASF.
SRP	is soil release polymer (Texcare SRN 170 ex Clariant)
Dequest® 2066	is Diethylenetriamine penta(methylene phosphonic acid (or Heptasodium DTPMP) ex Thermphos
Perfume	is free oil perfume.

The fabric conditioner

[0120] The fabric conditioner used for the examples was a commercially available concentrated fabric conditioner composition sold under the "Comfort" brand in the UK and based on Hardened Tallow TEAQ. The formulation of the fabric conditioner is given in table 1. The fabric conditioner was used at the recommended dose for this concentrated fabric conditioner of 55mls.

Table 1 - Fabric conditioner composition

Ingredient	Amount %(100% active)
HTTEAQ	12.7
Stenol 1618L	1.00
Genepol C200	0.38
Perfume (free oil)	0.79
Minors and water Including preservative, anti-foam, pH modifier	To 100

The detergent liquids

[0121] Two prior art detergent liquids and 4 liquids suitable for use in the invention are set forth in tables 2 to 4. Compositions 1 to 4 for use in the invention are given in table 2. Comparative Composition A (Ariel Excel gel with Biological action) a commercially available detergent liquid sold in the UK is stated on pack to have the composition given in table 3. The pack further recommends that it is dosed at 37ml per wash. Comparative Composition B (Persil Small and Mighty Biological) a commercially available detergent liquid sold in the UK, has the composition given in Table 4. It is recommended to be dosed at 35ml per wash.

Table 2 - Compositions 1 - 4

	35ml dose liquids		20ml dose liquids	
Example	**1**	**2**	**3**	**4**
% active	24	17.1	24	17.1
Ingredient	**b**24%	**a**17.10 %	**b**24%	**a**17.10 %
MPG	20	20	20	20
TEA	0	0	0	0
Citric Acid	0	0	0	0
NaOH	1.5	1.01	2.625	1.7675
NI 7 EO	10.55	7.28	18.4625	12.74
LAS acid	7.02	4.85	12.285	8.4875
Fatty acid	2.46	1.7	4.305	2.975
SLES (3EO)	3.5	2.42	6.125	4.235
Empigen® BB	0.86	0.86	1.505	1.505
EPEI	3.1	3.1	5.425	5.425
SRP	2.1	2.1	3.675	3.675
Dequest® 2066	0	0	0	0
Perfume	1.39	1.39	2.4325	2.4325
Protease	1.35	1.35	2.3625	2.3625
Amylase	0.54	0.54	0.945	0.945
Mannanase	0.4	0.4	0.7	0.7

Table 3 - Comparative Composition A

Ingredient	Amount (%)
Anionic Surfactant	>30
Soap	5-15
Nonionic	<5
Water, phosphonates, optical brighteners, enzymes, perfume and minors	To 100

[0122] According to additional supplier (P&G) published information the surfactant system is believed to be made up from MEA-Dodecylbenzenesulfonate (LAS neutralised with MEA), Sodium Laureth Sulfate (SLES) and, MEA-Palm Kernelate.

[0123] In addition to water, the published information also suggests that the composition further includes: MEA Citrate, C12-14 Pareth-7 (nonionic/emulsifier), PEI-Ethoxylate, Trimonoethanolamine Etidronate, Propylene Glycol, MEA-Borate, Glycosidase, Sodium Sulfate, Disodium Distyrylbiphenyl Disulfonate, Ethanolamine, Protease, Calcium Chloride, Colorant, and perfume.

Table 4 - Comparative Composition B

Ingredient	Amount (%)
LAS acid	13.40
SLES(3EO)	6.70
NI 7EO	20.12

(continued)

Ingredient	Amount (%)
NaOH	2.70
TEA	3.23
Fatty acid	4.78
MPG	9.00
Glycerol	5.00
Dequest® 2066	0.50
Citric Acid	0.98
Optical Brightener	0.10
Protease	1.35
Amylase	0.54
Mannanase	0.40
Perfume (free oil)	1.39
Water and minors including colorant	To 100%

Example 1 - Performance Assessment

[0124] The experiment described below was designed to ascertain the impact of habitual rinse conditioner usage on stain removal in subsequent washes.

Table 5 - Products tested and dosage

Example	Dosage / ml
A	37
B	35
1	35
2	35

[0125] Washes were conducted in a European Miele washing machine using the standard 30°C cotton wash cycle. The main wash intake was 15 L of ambient temperature water of 26°FH water (Ca:Mg 3:1) and the total wash time (including rinses) was 1 hour 56 minutes. A mixed ballast load of 3 kg (40% woven polyester, 30% woven cotton, 30% knitted cotton) was also included in each cycle to better mimic real wash use conditions.

[0126] Two wash processes were used:

Process 1 - Prewash Treatment only

[0127] Each of the products in Table 5 was used to wash a ballast load as described above together with a series of cotton and polyester swatches that were to be subsequently stained. After washing all fabrics were tumble dried. After two complete wash cycles, the swatches were soiled using a range of soils. A final wash treatment was then conducted on the stained swatches using the same ballast and wash conditions as before.

Process 2 - Prewash and Rinse Conditioner Treatments

[0128] Each of the products in Table 5 was used to wash a ballast load as described above together with a series of cotton and polyester swatches that were to be subsequently stained. In this process, 55ml of the fabric conditioner detailed in Table 1 was added to the final rinse of each wash. After washing all fabrics were tumble dried. After two complete wash cycles, the swatches were soiled using a range of soils. A final wash treatment was then conducted on the stained swatches using the same ballast and wash conditions as before. No rinse conditioner was used after the final wash.

Assessment

[0129] After washing, the stained swatches were line dried in the dark before being assessed for stain removal.

[0130] Before and after washing the colour of the stains was measured on a flatbed scanner and expressed in terms of the difference between the stain and clean (washed) cloth giving ΔE*(before wash) or ΔE*(after wash) values respectively. The ΔE values being the colour differences defined as the Euclidian distance between the stain and clean cloth in L*a*b* colour space. The ΔE*(after wash) values were converted to Stain Removal Index (SRI) values by application of the standard transformation:

$$SRI = 100 - \Delta E^*(\text{after wash})$$

[0131] The impact of rinse conditioner treatment was determined by measuring the loss of performance of each composition tested product when used in conjunction with rinse conditioner (Process 2) relative to that in the absence of rinse conditioner (Process 1). Table 6 shows the SRIs without use of Rinse conditioner. Table 7 shows the revised SRI when rinse conditioner is used as part of the pretreatment and the change in SRI (Process 1 - Process 2) is given for the full set of stains in Table 8. KC means knitted cotton. KP means knitted polyester.

Table 6 - Stain removal -prewashing without Rinse conditioner (Process 1)

	A	B	1	2
Stain	**SRI Lsmeans**	**SRI Lsmeans**	**SRI Lsmeans**	**SRI Lsmeans**
Ragu/Sunflower Oil KP	99.4	98.6	98.8	98.6
Tomato (Pomarola) / Sunflower Oil KP	98.6	97.9	99.4	99.5
Red Pepper/oil/water KP	98.5	96.6	99.4	99.3
Red Curry (Osman) KP	98.8	98.0	99.6	99.5
Face Make-up 2 KP	99.2	99.1	99.2	99.3
1:1 Garden Soil : Water KC	87.4	87.0	87.3	87.2
Black Tea KC	88.2	82.1	82.3	82.5
Mechanical Grease KC	54.6	55.7	54.1	54.3
Cocoa / milk KC	96.2	90.9	87.9	87.8
Face Make-up 2 KC	94.2	91.5	92.0	90.2
Red Curry (Osman) KC	78.0	77.1	76.3	75.0
Yellow Pottery Clay 2:1 KC	82.8	80.5	79.8	77.6
Choc Pudding (Heinz) KC	92.8	92.2	92.0	91.7
Red Pottery Clay 2:1 KC	78.2	74.0	76.2	76.8
Choc Ice Cream (Economy) KC	92.7	86.7	86.9	87.3
Blood (haemoglobin) KC	87.6	86.3	85.5	85.7
Total of SRI values	1427.0	1394.1	1396.7	1392.3

Table 7 - Stain removal -prewashing with Rinse conditioner (Process 2)

	A	B	1	2
Stain	**SRI Lsmeans**	**SRI Lsmeans**	**SRI Lsmeans**	**SRI Lsmeans**
Ragu/Sunflower Oil KP	82.7	77.9	97.0	98.1
Tomato (Pomarola) / Sunflower Oil KP	89.7	89.0	99.3	99.4

(continued)

	A	B	1	2
Stain	**SRI Lsmeans**	**SRI Lsmeans**	**SRI Lsmeans**	**SRI Lsmeans**
Red Pepper/oil/water KP	89.9	84.4	99.4	99.3
Red Curry (Osman) KP	92.8	88.3	99.6	99.5
Face Make-up 2 KP	93.4	91.0	99.0	99.2
1:1 Garden Soil : Water KC	82.9	89.1	88.6	87.2
Black Tea KC	84.8	82.6	82.7	82.6
Mechanical Grease KC	53.0	58.1	54.9	57.2
Cocoa / milk KC	94.7	94.4	90.4	90.1
Face Make-up 2 KC	92.8	93.4	91.9	92.4
Red Curry (Osman) KC	76.7	76.3	77.1	77.6
Yellow Pottery Clay 2:1 KC	82.7	78.5	81.5	83.2
Choc Pudding (Heinz) KC	93.8	94.5	94.8	96.3
Red Pottery Clay 2:1 KC	79.3	78.9	79.8	83.6
Choc Ice Cream (Economy) KC	94.5	89.2	90.5	93.5
Blood (haemoglobin) KC	90.1	95.4	93.6	95.7
Revised Total of SRI values	1373.8	1360.9	1420.1	1434.7

Table 8 - Stain removal -Difference in SRI - ΔSRI

	A	B	1	2
Stain	**ΔSRI Lsmeans**	**ΔSRI Lsmeans**	**ΔSRI Lsmeans**	**ΔSRI Lsmeans**
Ragu/Sunflower Oil KP	-16.7	-20.7	-1.8	-0.5
Tomato (Pomarola) / Sunflower Oil KP	-8.9	-8.9	-0.2	-0.1
Red Pepper/oil/water KP	-8.6	-12.2	0.0	0.0
Red Curry (Osman) KP	-5.9	-9.7	0.0	0.0
Face Make-up 2 KP	-5.8	-8.0	-0.2	-0.1
1:1 Garden Soil : Water KC	-4.5	2.1	1.3	-0.1
Black Tea KC	-3.4	0.4	0.4	0.1
Mechanical Grease KC	-1.6	2.4	0.8	2.9
Cocoa / milk KC	-1.5	3.5	2.5	2.3
Face Make-up 2 KC	-1.4	1.9	-0.1	2.2
Red Curry (Osman) KC	-1.3	-0.7	0.8	2.6
Yellow Pottery Clay 2:1 KC	-0.1	-2.0	1.7	5.6
Choc Pudding (Heinz) KC	1.0	2.3	2.8	4.6
Red Pottery Clay 2:1 KC	1.1	4.9	3.6	6.8
Choc Ice Cream (Economy) KC	1.9	2.5	3.6	6.2
Blood (haemoglobin) KC	2.5	9.1	8.1	10.0
	-53.2	-33.3	23.4	42.4

[0132] Fatty/oily stains: Ragu/Sunflower Oil, Tomato (Pomarola) / Sunflower Oil, Red Pepper/oil/water, Red Curry (Osman), Face Make-up. Mechanical Grease

[0133] Particulate stains: 1:1 Garden Soil : Water, Yellow Pottery Clay 2:1, Red Pottery Clay 2:1

[0134] Sequestrant stains: Black Tea

[0135] Enzymatic stains: Cocoa / milk, Choc Pudding (Heinz), Choc Ice Cream (Economy), Blood (haemoglobin).

[0136] The data show that the compositions used according to the invention exhibit a much greater robustness to rinse conditioner presence than the prior art comparative compositions with higher in wash surfactant levels. Where there are reductions in performance on adding conditioner, these are reduced. Where there are benefits on adding conditioner, these are amplified. There are several significant wins with oily/fatty stains on Polyester. There is approximate parity on enzymatic and particulate stains. The performance on sequestrant stains is unexpectedly as good as, or better, than the comparative compositions.

[0137] Looking at Composition 2 versus comparative composition B: there are significant wins with oily/fatty stains, especially on Polyester. There are significant wins on particulate stains and there is parity on enzymatic/ bleachable/ sequestrant stains. The effects are biggest with Oily/Fatty stains on Polyester.

[0138] Composition 2 versus Comparative composition A shows superiority with fatty/oily stains on polyester. The same slight downward trend as compared with B is observed on cotton (2 significant results). Enzymatic and particulate stains give approximate parity.

[0139] When the higher surfactant levels used in Composition 1 are compared with the results obtained for Composition 2 the benefit of using the lower in-wash non soap surfactant levels is seen. Composition 2 is outperforming composition 1 when used after rinse conditioner.

Claims

1. A method of laundering fabric onto which a cationic fabric softening active has been deposited and dried comprising the step of contacting the fabric with an aqueous wash liquor having the following composition:

    a) 15 to 600 ppm non-soap surfactant,
    b) at least 50 ppm ethoxylated polyethylene imine,
    c) at least 25 ppm polyester soil release polymer,
    the total level of polymer (b+ c) being at least 20 wt% of the level of non soap surfactant (a),
    d) 0.1 to 100 ppm enzyme selected from protease, amylase, cellulase,
    e) optionally, lipase enzyme.

2. A method according to claim 1 in which the level of non-soap surfactant (a) is from 200 to 400 ppm.

3. A method according to any preceding claim in which the non-soap surfactant (a) comprises at least 50 ppm of anionic surfactant.

4. A method according to any preceding claim in which the EPEI is nonionic.

5. A method according to any preceding claim in which the cationic fabric softening active is a quaternary ammonium compound.

6. A method according to any preceding claim in which the polyester soil release polymer (c) is nonionic and comprises a polyester substantive midblock of terephthalate repeat units and one or more end blocks of polyethylene glycol capped with a lower alkyl or hydrogen moiety.

7. A method according to any preceding claim in which the wash liquor is formed by dosing 15 to 40 ml of an aqueous liquid detergent composition to water and diluting by a factor of at least 600.

8. A method according to any preceding claim in which the non-soap surfactant comprises LAS, SLES and ethoxylated fatty alcohol nonionic.

9. A method according to any preceding claim in which the non-soap surfactant comprises carbobetaine.

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EUROPEAN SEARCH REPORT

Application Number
EP 11 16 0937

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A,D	WO 2009/153184 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; UNILEVER HINDUSTAN [IN]) 23 December 2009 (2009-12-23) * pages 33-39; examples 2-5,21-31 * * pages 42-44; claims * -----	1-9	INV. C11D3/00 C11D3/37 C11D3/386 C11D11/00
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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	23 August 2011	Pfannenstein, Heide

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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